

Review

# Nitrogen-doped carbon nanostructures and their composites as catalytic materials for proton exchange membrane fuel cell

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## Abstract

The research and development of catalysts with high activity and high durability is a significant issue for proton exchange membrane fuel cell (PEMFC). Nitrogen-doped carbon nanostructures and their composites demonstrate promising potential for PEMFC catalysts application. The nitrogen doping strategies of carbon nanostructures and the electrocatalytic aspects of nitrogen-containing carbon with and without catalytic metals on it are reviewed. Pt-based catalysts with nitrogen-doped carbon as support exhibit enhanced catalytic activity and durability toward oxygen reduction and methanol oxidation, which can be attributed to the high dispersion of Pt nanoparticles and the modified interaction between Pt nanoparticles and the support. For most of the non-Pt metal catalysts (Fe, Co, etc.) presently investigated for potential application in PEMFC, nitrogen is the indispensable element, and even though there are still controversies, the pyridinic type nitrogen is generally considered to be responsible for the catalytic sites. But the catalytic activity is still low and the stability issue is another challenging problem for non-Pt metal catalysts. Nitrogen-doped carbon, without catalytic metals on it, also shows enhanced catalytic activity. But many issues still need further investigation in order to get catalysts with targeted activity and durability.

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**Keywords:** Proton exchange membrane fuel cell; Nitrogen doping; Carbon nanostructures; Non-Pt catalysts; Oxygen reduction; Durability

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## 1. Introduction

Due to the attractive system efficiencies and environmental benefits, fuel cells have been attracting much attention as an alternative power generation in 21st century. Among all the

various kinds of fuel cells [1], proton exchange membrane fuel cell (PEMFC) is believed to be the main candidate power source for next-generation light-duty vehicles because of its fast startup and immediate response to changes in the demand for power. It has also shown great promise for mobile applications such as portable electronics. However, the commercialization of PEMFC has been proved to be difficult to achieve [2]. One of the main problems encountered in its commercialization is the prohibitive cost of component materials (the membrane, the bipolar plate, the catalyst

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(presently carbon supported Pt and its alloys), etc.) [3–6]. The production cost of certain component materials, such as membranes and bipolar plates, is expected to be greatly decreased by the economies of scale (i.e., the mass production) [7], but it might be not true for catalysts in light of the probable upward pressure on Pt price, a limited natural resource of Pt [8], as volume increases [9]. So it is a prerequisite to decrease the usage of Pt, which requires to increase the mass specific activity of the catalyst, or to find an alternative non-noble metal catalyst that can give an acceptable catalytic performance [10], in order to achieve a competitive low cost of fuel cell. Other problems of present PEMFC include low material durability [11–13] and system reliability [14].

It is generally believed [15,16] that metal catalysts should be deposited on porous nanostructure materials in order to increase the specific surface area, which is the prerequisite to obtain an acceptable catalytic performance (gauged in the activity per gram metal). The surface chemistry and the structure of the support materials can greatly influence the activity of the resultant catalysts. This is because the interaction between the support and metal catalyst can modify the electric structure of catalytic metals which in turn changes the catalytic activity [4,17–19], and the durability of the resultant catalysts depends on the metal-support interaction and the durability of the support materials [11,12,20].

Carbon is an ideal support for electrocatalysts for PEM fuel cell [21]. In fact, no other material except carbon has the essential properties of high electronic conductivity, corrosion resistance, surface properties, easy reclaim of precious catalytic metals and the low cost. In general, the conventional support carbon black (Vulcan XC-72) is used for the dispersion of Pt nanoparticles. The appearance of novel carbon support materials, such as graphite nanofibers (GNFs) [22,23], carbon nanotubes (CNTs) [4,11,17,24–29], carbon nanohorns [30] and carbon nanocoils [31–34], provides new opportunities of carbon supports for PEM fuel cell applications. They have shown promising results towards fuel cell electrode reactions: oxygen reduction reaction (ORR) and the electrochemical oxidation of small organic molecules (methanol, alcohol, dimethyl ether) [17,28]. But, in terms of activity, cost and durability, current catalysts can still not satisfy the requirements of target PEMFC [2,3,7,35]. So people are striving to find novel catalyst materials (both the catalytic metals and support materials). These efforts include: (i) to increase the specific activity of Pt-based materials by alloying Pt with other metals, developing novel structure of Pt (porous Pt, Pt-skin structure [36,37], core-shell structure [38]) and so on; (ii) to find out non-Pt metal catalysts [39,40]; (iii) to find out novel support materials through modern advance in nanoscience and nanotechnology. Usually the (iii) strategy is employed together with the first two strategies.

One approach to find a novel support is to dope porous carbon nanostructure materials with nitrogen. As is known, carbon nanostructure materials (e.g., CNT, CNF) have shown already promising potential applications in many fields [41,42]: electronics, sensors, polymer composites, hydrogen storage, catalysis and electrodes, due to their unique structures at the

molecular and nanoscale levels [41]. Doping carbon nanostructures adds another dimension to these structures' properties [43–47]. Doping of carbon can affect such properties as pH, catalytic activity, conductivity and nanostructure. Nitrogen-doped carbon nanotubes/nanofibers (N-CNT/N-CNF) with metal catalysts or without metals on them show enhanced catalytic activity toward oxygen reduction reaction (ORR) [48–50], which is the Holy Grail in the fuel cell community, because the over-potential loss due to the slow reaction kinetics of ORR is more than quarter of the total ideal electrode potential, which greatly decreases the energy efficiency, the specific power and energy density of a fuel cell. Nitrogen-doped carbon as the catalyst support is also expected to improve the durability of the resultant catalysts, because of the enhanced  $\pi$  bonding [11,51,52] and the basic property [53], due to the strong electron donor behavior of nitrogen [43,54,46,55].

The research and development of nitrogen-doped nanostructured carbon and their composite as potential catalytic materials for PEM fuel cell in recent past years are reviewed based on selected research reports from peer-reviewed journal publications. This review article consists of the following sections: (i) the nitrogen-doping method of carbon nanostructure materials, (ii) Pt-based catalysts with N-carbon as the support, (iii) the alternative non-noble metal catalysts based on N-carbon, (iv) the inherent catalytic activity of N-carbon (without metals on it).

## 2. Nitrogen doping methods

Nitrogen doping of carbon nanostructure materials can be categorized into two categories [42]: (i) doping directly during the synthesis of porous carbon nanostructure materials, which can be called as “in situ” doping; (ii) post-treatment of pre-synthesized carbon nanostructure materials with nitrogen-containing precursor ( $N_2$ ,  $NH_3$ , etc.), i.e., post-doping.

The “in situ” doping method is often used in nitrogen-doped carbon nanotubes (N-CNT) and nitrogen-doped carbon nanofibers (N-CNF). Several reviews have been recently published on nitrogen-doped carbon, especially on nitrogen-doped carbon nanotubes [42,56]. Several methods can be employed to synthesize nitrogen-doped carbon nanotubes [42], which are similar to those used to synthesize pure carbon nanotubes [57–61]: (i) high-temperature synthesis methods such as arc-discharge [62,63] and laser ablation [64,65]; (ii) low-temperature synthesis methods such as chemical vapor deposition (CVD) [66,67]. CVD and other modified CVD methods (aerosol assisted CVD [68,69], floating catalyst CVD [70], microwave plasma enhanced CVD [71], pyrolysis-type CVD [46,66,72–74]) might be the most popular and economically competitive to produce nitrogen-doped carbon nanotubes; (iii) solvothermal synthesis method, which seems to produce stable large diameter nanotubes with very high nitrogen contents [75,76].

Post-treatment of carbon materials in nitrogen-containing atmosphere can also form N-doped carbon. Most of the post-dopings are carried out in  $NH_3$  at high temperatures (600–900 °C) [48,77–79]. Jiang and Gao's research [77] showed that

it generated basic nitrogen-containing groups (e.g., amine) on the nanotubes, which are hydrophilic to make the CNTs disperse easily in aqueous medium. Sidik et al. [48] reported an enhanced electrocatalytic activity toward oxygen reduction on  $\text{NH}_3$ -treated carbon, but there are still controversies on this topics [80].

In some cases, carbon nanostructure materials with ordered structure are preferred [46,81–83], for example, fuel cell electrodes with ordered structure provide the advantages of enhanced electron conductivity and the mass transport [21,24]. Many researches are carried out on ordered carbon nanostructure materials (CNT/CNF) [84–86]. There are two synthesis strategies for ordered nitrogen-doped CNTs/CNFs: the substrate-growth and the template-growth. All these methods are similar to those used in the growth of pure aligned CNTs/CNFs [58–61,82,83,85,87–89]. Most of the methods used in fabricating ordered N-CNT or N-CNF are the “in situ” ones, i.e., doping is carried out during the formation of ordered CNT or CNF.

In the substrate-growth of N-CNTs/N-CNFs via CVD, the process usually involves heating a catalyst material in a furnace and flowing carbon and nitrogen precursors through the tube reactor for a period of time. The catalytic species are transition metal nanoparticles which are previously supported on the substrate materials. Simplistically, the catalyst particles serve as seeds to nucleate the growth of N-CNTs/N-CNFs. The widely used transition metal catalysts are Fe [90,91], Ni [92,93], Co [24,92,94], etc. They can be deposited onto the substrate materials by sputtering, electrochemical deposition [24], pyrolysis of metal precursors (e.g., ferrocene ( $\text{Fe}(\text{C}_5\text{H}_5)_2$ ) [90,95]). The substrate might be quartz plates [90,95,96] or Si wafers [90,93,97]. The metal catalysts might be deposited on the substrate prior to the growth of N-CNTs or in situ formed during the growth of N-CNTs (i.e., the precursors of carbon, nitrogen and metal catalyst are mixed and simultaneously flowed into the reactor [90,95,96]). Park and co-workers [97,98] also reported the aligned N-CNTs synthesized via pyrolysis of chemicals containing all the catalyst metal, nitrogen and carbon, i.e., iron phthalocyanine ( $\text{FeC}_{32}\text{N}_8\text{H}_{16}$ , FePc), cobalt phthalocyanine (CoPc) and nickel phthalocyanine (NiPc).

In recent years, many efforts are devoted on the template-growth of N-CNTs [89,99]. Xia and Mokaya [84] reported well-ordered porous N-doped carbon materials (CNx with N content of ~8.5%) that possess graphitic pore walls prepared via conventional CVD and pyrolysis at 950–1100 °C with the pure silica SBA-15 or other mesoporous silicas as solid templates. Hou et al. [100] reported a nitrogen-containing microporous carbon with a highly ordered structure synthesized by using zeolite Y as a template, which is found to be efficient to obtain N-CNTs with both high microporosity and ordering. Nitrogen-containing carbon nanotubes prepared by template synthesis using precursors such as polyvinyl pyrrolidone (PVP) [101], polyacrylonitrile [82] and polypyrrole [102], have also been reported. Anodic aluminum oxide (AAO) is also often used as the template for the synthesis of N-CNTs [101,103]. With the template-growth method, people can obtain N-CNTs with

various carbon layers modified with nitrogen. Kyotani and co-workers [103,104] reported carbon nanotubes with a double coaxial structure of nitrogen-doped and undoped multiwalls prepared with template technique. It involves two-step CVD of precursors with AAO film as a template. It can be determined whether the N-doped layer belongs to the inner or outer multiwalls by changing the sequence of the two-step CVD process [103]. Moreover, the thickness of both the N-doped and pure carbon layers is controllable by changing each CVD period. The N-doped layer has apparently higher chemical reactivity toward oxygen than the undoped one due to more edge-active sites resulting from the introduction of nitrogen species [104]. Electrical conductance measurement indicates that, despite poorer crystallinity, the N-doped layer has higher conductivity than undoped one [104]. This is due to the nature of n-type doping [44] and the strong electron donor states near the Fermi level [54], which is also confirmed by quantum chemical calculations [105].

It has been shown that, like in the case of CNT preparation [106–109], the structure and the properties of N-CNT/N-CNF are influenced by the catalyst, the precursors, even the CVD temperature [110–112]. The Ni-derived fibers generally have much thinner walls relative to the total fiber diameter compared to the Fe-derived samples [113]. Moreover, the Ni-grown fibers are generally longer, probably because they are not composed of many small compartments such as the Fe-derived materials, which appear to break apart easily [113]. And small Ni nanoparticles (<6 nm) catalyze the growth of the single-walled carbon nanotube (SWNT) through the base growth mode; larger Ni nanoparticles (7–30 nm) tend to form mostly multi-walled carbon nanotube (MWNT)/bamboo-like carbon nanotube (BCNT) [109]. Nitrogen concentration in N-CNT can reach as high as 10–20 at.% when acetonitrile or DMF was used as precursors [69,72], while, in the case of pyridine as precursor, only 1–2 at.% nitrogen can be doped into CNT [96], and nitrogen content ranges from 4.8 to 8.8 at.% when  $\text{NH}_3$  was used as precursor [95]. It is summarized in Table 1. It also suggests that not only nitrogen concentration, but also nitrogen doping nature of carbon nanotubes can be controlled by changing the growth temperature or flow rate of  $\text{NH}_3$  [95], for example, the proportion of pyridine-like structure decreases with increasing growth temperature under pure  $\text{NH}_3$  atmosphere, while the pyridine structure increases with increasing the flow rate of  $\text{NH}_3$  [95]. The nitrogen content in N-CNTs in turn influences the nanostructures, with lower nitrogen content favorable for producing linear products [114]. And N-CNTs always have a so-called ‘bamboo’ structure. The alignment and number of nanotube walls depends on dopant concentration and catalyst used [42]. More information about the synthesis and the structure of N-CNT can be found in refs. [42,115].

### 3. Pt-based catalysts

Pt-based electrocatalyst with porous carbon black as support material is still the only practical catalyst in present PEM fuel cells, which is still in need of further improvement in terms of catalytic activity and durability [2,9,13]. Both of the experi-

Table 1  
Nitrogen-doping methods and nitrogen concentration on carbon nanostructure materials

Methods	Catalysts	Precursors	N content (%)	References
HT		NH <sub>3</sub>	N/A	[48]
Pyrolysis	Fe	Melamine (C <sub>3</sub> H <sub>9</sub> N <sub>6</sub> )	<7	[46]
Pyrolysis	Ferrocene (Fe(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> )	Melamine (C <sub>3</sub> H <sub>9</sub> N <sub>6</sub> )	10	[66]
AA-CVD	Ferrocene (Fe(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> )	Benzylamine (C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> NH <sub>2</sub> )	<5	[68]
AA-CVD	Fe <sup>0</sup> from Fe(III) (acetylacetonate) <sub>3</sub>	Acetonitrile (CH <sub>3</sub> CN), tetrahydrofuran (C <sub>4</sub> H <sub>8</sub> O)	20	[69]
FC-CVD	Ferrocene (Fe(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> )	Pyridine/xylene/NH <sub>3</sub>	10	[70]
MPE-CVD	Fe	CH <sub>4</sub> /N <sub>2</sub>	15–17	[71]
Pyrolysis	Fe	Dimethylformamide (HOCN(CH <sub>3</sub> ) <sub>2</sub> )	2–16	[72]
Pyrolysis	Co	2-Amino-4,6-dichloro- <i>s</i> -triazine (C <sub>3</sub> N <sub>3</sub> Cl <sub>2</sub> NH <sub>2</sub> )	1–2	[74]
HT	No	NH <sub>3</sub>	0.7	[78]
HT	Fe	NH <sub>3</sub>	2–4	[79]
FC-CVD	Ferrocene (Fe(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> )	C <sub>5</sub> H <sub>5</sub> N	2.6	[90]
Pyrolysis	Fe	Melamine	4–5	[91]
Pyrolysis	Ni/Co	Acetonitrile	0.5–1.2	[92]
Pyrolysis	Co	Pyridine	2	[94]
pyrolysis	Ferrocene (Fe(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> )	NH <sub>3</sub>	4.8–8.8	[95]
CVD	Ferrocene (Fe(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> )	Pyridine (C <sub>5</sub> H <sub>5</sub> N)/pyrimidine (C <sub>4</sub> H <sub>4</sub> N <sub>2</sub> )	1–3	[96]
Pyrolysis		FePc/CoPc/NiPc	0.7–7.8	[97]
CVD		Acetonitrile	8	[99]
Pyrolysis		C <sub>3</sub> H <sub>6</sub> /CH <sub>3</sub> CN	3.2–3.5	[103]

Note: HT, Heat treatment; AA-CVD, aerosol assisted CVD; FC-CVD, floating catalyst CVD; MPE-CVD, microwave plasma enhanced CVD.

mental and theoretical studies have shown that Pt-based metals supported on nitrogen-doped carbon nanostructure materials are promising potential catalysts for PEMFC [116]. In the past years, great progresses have been made in this field.

Sun et al. [50] reported aligned N-CNTs supported Pt nanoparticles with useful catalytic applications in micro direct methanol fuel cell ( $\mu$ -DMFC). The aligned N-CNTs were grown on iron-coated Si substrate by microwave-plasma-enhanced chemical vapor deposition (MPECVD) with the mixtures of CH<sub>4</sub>, N<sub>2</sub> and H<sub>2</sub> as source gases. Two types of nitrogen were observed from XPS analysis of the N-CNTs, one is substitution-type nitrogen bonding in the graphite layer of the NT wall, the other is pyridine-type nitrogen. Pt nanoparticles with an average diameter of 2 nm and a high dispersion were deposited on N-CNTs by sputtering method. The authors [50] attributed the small diameter and high dispersion of Pt nanoparticles to the fact that the sputtered Pt atoms were confined by the capture sites, among which the substitutional nitrogen sites might provide the main initial nucleation sites for the formation of Pt nanoparticles [117,118]. The deep-seated chemistry for favorable Pt deposition on N-CNT is probably due to the fact [85,100] that the introduction of N atoms endows the carbons with a polar nature, which makes it easy to wet [119]. This is confirmed in N-CNT/H<sub>2</sub>O system [85,100,119]: the nitrogen-containing carbon has a higher affinity to H<sub>2</sub>O molecules than the nitrogen-free carbon. Sun's work provides a possible method to efficiently deposit Pt nanoparticles on hydrophobic nanostructured carbon, since most carbon is not favorable for Pt deposition [120] which often results in large particle size and poor dispersion of metals [32].

Maiyalagan et al. [21] reported aligned N-CNT supported Pt nanoparticles with an average size of 3 nm for methanol oxidation. The aligned N-CNTs were synthesized using the alumina membrane (Anodisc 47) as template and polyvinyl-

pyrrolidone (PVP) as N–C precursor. They observed an enhanced catalytic activity and stability toward methanol oxidation on Pt/N-CNTs as compared with commercial E-TEK Pt/Vulcan by measuring the onset potential for methanol oxidation (0.22 V versus 0.45 V, Ag/AgCl) and the forward peak current density in cyclic voltammogram (CV) (13.3 mA cm<sup>−2</sup> versus 1.3 mA cm<sup>−2</sup>). The enhanced electrocatalytic activity of Pt/N-CNTs was tentatively attributed the following factors which still require further investigation: (1) higher dispersion of Pt nanoparticles on the N-CNTs (shown in Fig. 1) increases the availability of an enhanced electrochemically active surface area, (2) appearance of the specific active sites at the metal–support boundary and (3) strong and specific metal–support interaction. The authors proposed that

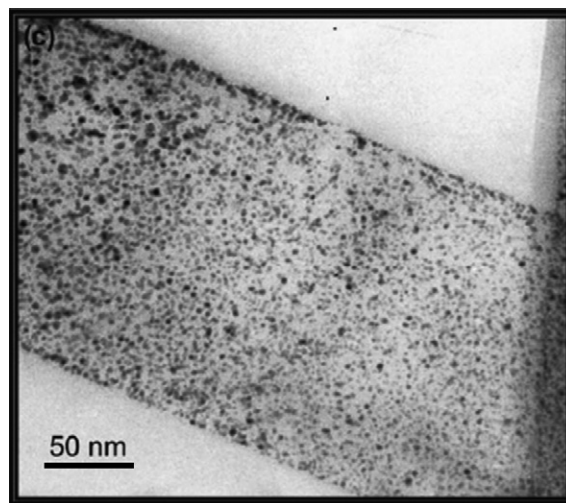


Fig. 1. TEM image of nitrogen-containing carbon nanotube supported Pt nanoparticles (ref. [21]).



the nitrogen functional groups on CNT surface intensify the electron withdrawing effect against Pt and the decreased electron density of platinum facilitates the oxidation of methanol. They also pointed out that the Vulcan carbon black support has randomly distributed pores of varying sizes which might make mass diffusion difficult whereas the tubular three-dimensional morphology of N-CNTs makes it easier. The Vulcan carbon black contains high levels of sulfur (ca. 5000 ppm or greater), which could potentially poison the fuel cell electrocatalysts [121], but N-CNTs are free from sulfur.

Post-treatment of carbon support with nitrogen can also increase the catalytic activity. Roy et al. [78] studied the effect of the nitrogen-doping of carbon black on the catalytic activities of the resultant catalysts toward oxygen reduction and methanol oxidation. Carbon black was first treated in CO<sub>2</sub> at 800 °C for 24 h to create oxygen functionality on the carbon surface and then in NH<sub>3</sub> at 800 °C for another 24 h. The treated carbon black was then catalyzed with Pt. Catalysts functionalized with nitrogen exhibited enhanced catalytic activities toward oxygen reduction and methanol oxidation as compared with the untreated ones. It was found that carbon supports functionalized with nitrogen initiated the formation of Pt particles with a smaller size than those observed on untreated carbon supports. The pH measurement indicated that nitrogen functionalization increased the basicity of the carbon support. The authors also proposed that the nitrogen functionality of the carbon support appears to play a role in determining the size of Pt nanoparticles and provide lone pairs of electrons at the nitrogen site in an sp<sup>2</sup> orbital in the plane of carbon ring. These nitrogen sites are less electronegative than the oxygen sites which predominate in untreated carbon black. During the catalyzation the platinum may bind more strongly to pyridinic sites, thereby preventing Pt particles from sintering. This is also found in coating Ag nanoparticles onto nitrogen-doped multi-walled carbon nanotubes [122]. Furthermore, the increased electron donation from pyridinic nitrogen functionality to Pt is considered to be responsible for the enhancements of the kinetics of both oxygen reduction and methanol oxidation [78].

#### 4. Non-Pt metal catalyst

Pt is an extremely expensive metal of low abundance, and hence, finding a non-noble metal alternative is of great interest and significance for fuel cell development. This is possible, provided that the alternative catalyst displays activity and stability approaching that of Pt [123]. The investigation on non-Pt metal catalysts for PEMFC is currently active with the cost consideration and other drawbacks of Pt-based catalysts [39,40], in terms of the selectivity for four-electron versus two-electron reduction of oxygen to H<sub>2</sub>O versus H<sub>2</sub>O<sub>2</sub> [39], the tolerance to impurities (CO, H<sub>2</sub>S, NH<sub>3</sub>, NO<sub>x</sub> and SO<sub>x</sub>) in fuel and oxidant [124], and the issues related with methanol at both anode [125,126] and cathode [127,128] for DMFC. Many elements and the compounds have been tested as potential catalysts, for example, refs. [39,40], transition metal chalcogenides (Mo<sub>4</sub>Ru<sub>2</sub>Se<sub>8</sub>, RuxMoySe<sub>z</sub>, RuxSy), transition metal

N<sub>4</sub>-macrocycles compounds (porphyrin complexes: N<sub>4</sub>-Fe, N<sub>4</sub>-Co). Even though no significant breakthroughs so far in non-Pt metal catalysts [3,130], promising results have been reported [10,80], which are recently reviewed [39,40,130,131]. In this section, we only focus on the development of nitrogen-containing non-Pt metal catalysts during the near past years from peer-reviewed journal publications, which are selectively summarized in Table 2.

Nitrogen-containing non-Pt metal catalysts for PEMFC are often obtained [129,132] by pyrolyzing transition metals (e.g., Fe, Co) precursors and nitrogen precursors at high temperature (600–900 °C), which were adsorbed on a carbon support. The metal precursors currently under investigation include [133,134]: (i) metal (Fe/Co) salts [80], such as Fe acetate [123,135], cobalt sulfate [136]; (ii) metallic complexes like ferrocene [137,138], iron phenanthroline [139] and Prussian blue related complexes [140,141]; (iii) N<sub>4</sub>-macrocyclic complexes like iron phthalocyanine [142–149], iron porphyrin [150,151] and cobalt tetraazaannulene [41,49,80,152,153]. The precursor of N might be either NH<sub>3</sub> [132,135,154] or CH<sub>3</sub>CN [129,136,138] or other N-containing molecules. As most organometallic complexes contain also nitrogen atoms, which are used in the metal coordination, these metal precursors are nitrogen precursors as well. It has been shown that the electrocatalytic activity toward ORR depends on [155]: (i) the nature of the metal and its precursor as well as the nature of the nitrogen precursor; (ii) the pyrolysis and/or post-treatment temperature and (iii) the metal loading on the carbon support. For example, Fe-based catalysts displayed the highest performance for ORR in acid [156] and increasing Fe content increases the concentration of the catalytic sites until all nitrogens of the phenanthroline type are coordinated with Fe [80,157,158]. These factors determine the catalytic site density and the turnover frequency (TOF), both of which determine the catalytic activity [3,131].

Nitrogen precursors are also critical to catalytic activity [39]. Nitrogen-containing chemicals as stated above such as polyacrylonitrile, tetracyanoquinodimethane, ethylenediamine, 1,2-phenylenediamine, hydrogen phthalocyanine, pyrrole and their derivatives have been found to be the effective precursors for catalyst preparation [159–161]. N-containing gases such as NH<sub>3</sub> [156] or acetonitrile [135], and N groups on a modified carbon support (e.g., HNO<sub>3</sub>/NH<sub>3</sub>-treated carbon support [162]) were also employed as the nitrogen sources for the preparation process). It has been demonstrated [156] that nitrogen on the surface of the carbon supports was an essential requirement to obtain non-noble metal-based catalytic sites. It was found [123] that the activity of the catalysts varies greatly with different carbon support, but neither the specific surface area of the catalysts nor the distribution of their macro- or mesopores is a determining factor for the catalytic activity. The most important factor is the N content of the materials [132]; the higher the N content, the higher the density of the catalytic sites and the better the electrocatalyst. The correlation between the increased nitrogen content and the increased catalytic activity is verified by Dodelet and co-workers in Fe-based ORR catalysts [129]. The selectivity of oxygen reduction to water (i.e., four-electron

Table 2  
Nitrogen-containing non-Pt catalysts for oxygen reduction reaction (ORR) for potential application in PEMFC

Catalysts	Methods	Main results and conclusions	References
Fe/C(N), Ni/C(N)	Pyrolyzing acetonitrile or acetate salt of Fe/Ni over Vulcan XC-72	Fe precursor adsorbed on the support before the pyrolysis produces the most active catalyst	[49]
Fe/C(N)	Pyrolyzing iron(II) acetate on carbon in an atmosphere containing NH <sub>3</sub>	The most important factor for catalytic activity is the N content; three catalytic sites: an iron oxide site, FeN <sub>4</sub> /C and FeN <sub>2</sub> /C, with the last site being the most active for ORR	[123]
Fe/C(N)	Pyrolyzing iron acetate (FeAc) on various carbon supports in NH <sub>3</sub> /H <sub>2</sub> /Ar	Disorganized carbon as support results in better catalysts for ORR and methanol resistance	[129]
FeCo/C(N)	Heat treatment of K <sub>3</sub> Fe(CN) <sub>6</sub> , K <sub>3</sub> Co(CN) <sub>6</sub> with carbon black under an inert atmosphere	The combination of Fe and Co incorporated at neighboring sites gave the highest activity to ORR and resistance to methanol	[139]
Fe/C(N)	Pyrolyzing Fe acetate or Fe porphyrin adsorbed on carbon in H <sub>2</sub> /NH <sub>3</sub> /Ar	Fe acetate as Fe precursor is beneficial for the formation of catalytic sites FeN <sub>2</sub> /C, which is more active than FeN <sub>4</sub> /C	[155]
Fe/C(N)	Pyrolyzing PTCDA combined with FeII acetate or Cl-FeTMPP and/or NH <sub>3</sub>	Increasing Fe content beyond a certain value (2 wt.% Fe as Cl-FeTMPP and 0.2 wt.% Fe as Fe acetate) will not increase the activity, because it mainly generates catalytically inactive Fe clusters	[158]
Fe/C(N)	Pyrolyzing Cl-FeTMPP or Fe acetate adsorbed on PTCDA or on prepyrolyzed PTCDA	The FeN <sub>2</sub> /C catalytic site exhibits higher catalytic activity and the selectivity for ORR (H <sub>2</sub> O vs. H <sub>2</sub> O <sub>2</sub> ); peroxide (H <sub>2</sub> O <sub>2</sub> ) degrades the catalysts	[164]
Fe/C(N)	Pyrolyzing iron(II) phthalocyanine (FePc)	Nitrogen doping improves the inherent electrical and electron transfer of CNF and the electrocatalytic activity for ORR	[167]
Fe <sub>x</sub> C <sub>1-x</sub> N <sub>y</sub> , Co <sub>x</sub> C <sub>1-x</sub> N <sub>y</sub>	Combinatorial sputter deposition and annealed at high temperature of catalyst film	Annealing increases the activity together with the structure transformation from the homogenous to the heterogeneous; films annealed at 800 °C were the most stable and the highest of catalytic activity; higher temperature annealing releases N	[169,170]

Note: PTCDA, Perylene tetracarboxylic dianhydride; Cl-FeTMPP, Cl-FeIII tetramethoxyphenyl porphyrin.

reduction of oxygen to water versus two-electron reduction to H<sub>2</sub>O<sub>2</sub>) is also increased on the catalysts with a larger surface concentration of nitrogen atoms [163,164].

It should be pointed out that carbon support also plays a more significant role in non-Pt metal catalysts than in Pt-based catalysts, the latter acts mainly as a high surface area support [155]. In the case of non-noble catalysts, carbon acts not only as a support but also a part of the active sites [129,165]. This is because the metal (iron or cobalt) is bound to nitrogen atoms, which themselves are bound to the carbon graphitic structure [129]. The type of nitrogen–carbon bonds and the geometry of the carbon surrounding these bonds define the overall M–N–C (M, metal) site and rules whether this site is active or not for ORR. So the nature of M–N–C bond, i.e., the chemistry of the metal and the chemical composition of the carbon surface, is the key for a catalyst to obtain a high catalytic activity for ORR [123,132,163,164].

It was observed [132,143,164,166] that there are usually two kinds of catalytic sites (labeled as FeN<sub>4</sub>/C and FeN<sub>2</sub>/C) in Fe-based catalysts, irrespectively of the Fe precursors used in catalyst preparation. The two catalytic sites are in different relative proportions depending upon the precursor. The difference in the structure of the two catalytic sites can be summarized as follows [155]: FeN<sub>4</sub>/C is an iron ion coordinated to four nitrogen atoms of the pyrrole type, themselves bound to the carbon support; FeN<sub>2</sub>/C is an iron ion coordinated to two nitrogen atoms of the pyridinic type, themselves bound to the carbon support. Even so, the complete coordination of the iron ion in that catalytic site still needs further investigation.

There is also difference in catalytic activity and selectivity for ORR between the two kinds of catalytic sites (FeN<sub>4</sub>/C versus FeN<sub>2</sub>/C) [123,155,158]. FeN<sub>2</sub>/C shows a higher activity and selectivity than FeN<sub>4</sub>/C. FeN<sub>2</sub>/C reduces oxygen with an apparent value of *n* close to the ideal value 4 (*n* is the number of electrons transferred during ORR) [164]). This is a desirable characteristic for cathode catalysts in PEMFC, which can greatly alleviate the formation of H<sub>2</sub>O<sub>2</sub> and increase the energy efficiency. The nature behind the activity of the two catalytic sites (FeN<sub>4</sub>/C versus FeN<sub>2</sub>/C) still needs further investigation.

Some researchers [43,167] believe that pyridinic nitrogen can be considered to be a marker for edge plane exposure since this type of nitrogen is only found on the edge of a carbon layer. Nitrogen-containing carbon structures with more edge plane exposure have noticeably more pyridinic nitrogen groups on the surface. It is likely that nitrogen plays an additional or separate role by improving the ability of graphitic sheets to donate electrons [43,48,55,168]. Therefore, the nitrogen content of the carbon is likely an important parameter, and it is also likely that an optimal composition of various nitrogen exists.

The nitrogen-containing non-Pt catalysts (Fe–C–N [169], Co–C–N [169,170]) for ORR can also be obtained by combinatorial sputter deposition. It was found that the nitrogen content of the as-sputtered library increases with Fe and Co content. Annealing these libraries resulted in a decrease in nitrogen content. The Fe–C–N library annealed at 800 °C displayed the highest activity but corresponds to neither a maximum nor a minimum in nitrogen content [169]. This is explained [169] by that annealing at 800 °C induces sufficient graphitization and retains a significant quantity of N to form a

substantial number of active sites, which is supported by the research of Hellgren et al. [171]: when sputtered CNx films are annealed above 500 °C, progressive graphitization and nitrogen loss occurs; above 800 °C, there is a preferential loss of pyridinic nitrogen.

Carbon particles can also be modified with polypyrrole to nitrogen-containing non-Pt catalysts for ORR [172]. Pyrrole was first electropolymerized on the surface of carbon black (CB). The resulting PPy/CB particle was then suspended into a solution of cobalt acetate in CH<sub>3</sub>OH, which was then refluxed for a sufficiently long time to allow accommodation of cobalt ions at the suitable site. The pristine CoPPy/CB catalyst showed moderate electrocatalytic activity for ORR. After heat treatment (700 °C under vacuum), the catalytic activity was enhanced, which can be observed from the positive shift of ORR onset potential on heat-treated CoPPy/CB. This is explained by the more closely packed Co-N<sub>4</sub> structure at the surface of the carbon support after the heat treatment: the shortening of the cobalt–cobalt distance allowing for O<sub>2</sub> molecules to bridge the two proximate cobalt centers.

The stability issue under PEMFC conditions is a great challenge for both Pt-based and non-Pt catalysts [13]. The origin of non-Pt catalyst instability in acid medium is mainly attributed to the product H<sub>2</sub>O<sub>2</sub> from the incomplete reduction of oxygen [131]. It is shown that even low peroxide levels of the order of 5 vol.% in H<sub>2</sub>SO<sub>4</sub> are able to decompose the catalytic sites releasing iron ions in the H<sub>2</sub>SO<sub>4</sub> solution [164]. The loss of catalytic activity correlates directly with the loss of iron ions by these catalysts [164]. With the co-existence of Fe/Fe<sup>2+</sup> and H<sub>2</sub>O<sub>2</sub>, which is known as Fenton's reagent [173], HO• could be formed, which is a much more ferociously oxidizing species, deleterious to both catalysts and polymer membranes in PEMFC. The heat treatment of the catalysts can improve the stability. But the problem is that, the loss of nitrogen cannot be avoided at high temperature [169,171,172] which results in the decrease in catalytic activity. It is necessary to optimize the heat-treating strategy. The other method is to decrease the amount of both H<sub>2</sub>O<sub>2</sub> and free Fe. It has been shown that the selectivity of H<sub>2</sub>O versus H<sub>2</sub>O<sub>2</sub> is enhanced on the catalytic site labeled FeN<sub>2</sub>/C [123,155,158]. So to increase the amount and the proportion of FeN<sub>2</sub>/C is expected to be an effective method to increase the catalyst stability.

## 5. Nitrogen-doped carbon (without catalytic metals)

Nitrogen-doped carbon cannot only work as the catalyst support, N-carbon itself (without catalytic metal on it) also shows enhanced catalytic activity towards ORR than carbon only. Some researchers referred that the metal (e.g., Pt, Fe, Co) is not required for ORR activity in nitrogen-doped carbon [174], even though N-carbon catalysts without metals show lower activity [113]. Instead, the metal particles may be acting as catalysts for the formation of active sites during the formation of N-carbon [49]. One way that metal particles could catalyze the formation of active sites is through the growth of carbon nanostructures with a specific architecture, for example, Fe particles might catalyze the growth of carbon

nanostructures with a higher percentage of the edge plane exposure [155,174], which have been widely believed to exhibit much higher activity towards ORR and many other electrocatalytic reactions [113], whether the precursor that is pyrolyzed is an organic macrocycle [167] or other C and N-containing species [49,52]. It has been shown [52] that N-doped CNF electrodes demonstrated improved electrocatalytic activity for ORR. In both neutral and alkaline pHs, the N-doped CNFs demonstrate over a 100-fold increase in catalytic activity for H<sub>2</sub>O<sub>2</sub> decomposition [52,175], which values (of catalytic reaction rates) are within an order of magnitude of decomposition rates reported for most active catalysts, e.g., Pt-black [176]. The authors attributed the observed enhanced activity to the presence of edge plane defects and nitrogen functionalities within the CNF structure [167]. It is observed that the sidewalls of the N-doped CNFs contain more dislocations and disruptions (disruptions and irregular curvature) in the graphene stacking (turbostratic disorder), which is due to the propensity of incorporated nitrogen to form pentagonal defects in the graphene sheets [177]. It is said that the introduction of nitrogen-containing pentagons into the basal planes disrupts the planar hexagonal arrangement of carbon atoms of graphite, which causes buckling of the graphene layers and results in interlayer distances fluctuating between wider and thinner distances than those in pristine graphite. The catalytic activity of N-CNFs toward ORR and H<sub>2</sub>O<sub>2</sub> decomposition is a direct result of nitrogen doping [52]. Nitrogen doping has repeatedly been reported to increase the basic nature [175,178,179] and catalytic activity [175,180,181] of the graphitic carbon.

But there is still controversies on this topic: Ozkan and co-workers [49] believed that, even though the most active catalyst had a significantly higher amount of pyridinic nitrogen, pyridinic nitrogen itself may not be the active site for ORR, but may be a marker for edge plane exposure (the plane in which pyridinic nitrogen is found), on which many electrocatalytic reactions show increased kinetics. It has been shown that the final product of ORR (H<sub>2</sub>O versus H<sub>2</sub>O<sub>2</sub>) is influenced by the plane where oxygen reacted. Oxygen could only be reduced to peroxide when it reacted on the basal plane of nitrogen-doped carbon [43,55] but could potentially be reduced further to H<sub>2</sub>O when it reacted at the edge [43,48,55,168]. In addition to being more active, the samples that had higher edge plane exposure were more selective for complete reduction of oxygen to water. This could possibly be explained by the modeling [48,182]. The most active nanostructures contain nitrogen and have higher edge plane exposure. The selectivity of the catalysts for complete oxygen reduction to water followed a trend similar to activity.

Radovic and co-workers [183] indicated that the enhanced basicity of carbon is a consequence of strong  $\pi$  electron delocalization in graphite carbon layers, which can be enhanced by nitrogen doping due to both the electron rich nature of nitrogen sites (e.g., pyridinic nitrogen possesses one lone pair of electrons in addition to the one electron donated to the conjugated  $\pi$  bond system) and the enhanced stability against oxidation of carbon which generally forms acidic oxygen-

containing groups [52]. Delocalized  $\pi$  electrons are capable of nucleophilic attack, imparting to the carbon a Lewis basicity independent of basic heteroatom functionalities. This is also confirmed with  $\text{pH}_{\text{pzc}}$  measurements (the pH where the net surface charge is zero) of nitrogen-doped carbons by Biniak et al. [175] and Maldonado et al. [70,184] which exhibit a basic nature ( $\text{pH}_{\text{pzc}} \sim 9$ ).

Mang et al. [185] showed that nitrogen incorporation produced activated carbons with increased stability toward oxidation. Strelko et al. [55] suggested that the strong Lewis basicity of N-doped carbons acts to facilitate reductive  $\text{O}_2$  adsorption at open circuit conditions without the irreversible formation of oxygen-containing functional groups. This has been experimentally verified by Boehm and co-workers [186] through observations of adsorbed  $\text{O}_2^{\bullet-}$  on ammonia-treated carbons that showed enhanced catalytic activity for oxidative reactions (i.e.,  $\text{NO}_2$ ,  $\text{SO}_2$ ). Maldonado and Stevenson [52] observed a strong correlation between the ORR peak potential and the nitrogen doping level: at a given scan rate, ORR peaks shifts about +30 mV per 1 at.% N incorporated.

The enhanced catalytic activity towards ORR was also found on carbon simultaneously doped with boron and nitrogen [187]. In nitrogen-doped carbon, it is inferred that either pyridinic or pyrrol/pyridone type nitrogen was responsible for the ORR activity of carbon [188]. In BN-doped carbon, the most probable candidate factor for the catalytic enhancement is the B–N–C moieties represented by N-II in N 1s XPS spectra and B-I and B-II in B 1s XPS spectra [187]. The exact roles of the nitrogen surface species and the B–N–C moieties are not clear at the present stage. It is possible that the roles of B and N are to change the surface properties such as hydrophilicity and basicity and to form active centers [187].

## 6. Conclusions and remarks

Nitrogen doping of nanostructured carbon is shown to be a promising strategy to obtain PEMFC catalysts with desirable performance. Nitrogen-doped carbon supported Pt-based catalysts exhibit enhanced catalytic activity and durability toward oxygen reduction and methanol oxidation. Nitrogen is the indispensable element in many non-Pt metal catalysts (Fe, Co, etc.) for potential application in PEMFC. The catalytic activity is still low and the poor stability is another challenging issue for non-Pt metal catalysts. Nitrogen-doped carbon, without catalytic metals on it, also shows enhanced catalytic activity.

For both the Pt and non-Pt catalysts based on nitrogen-doped carbon as support, many issues still need further investigation in order to obtain catalysts with targeted activity and durability, for example, the exact nature of the enhanced catalytic activity with N-doping, the interaction between the catalytic metals and different type of nitrogen atoms, the nature of the catalytic sites in non-Pt metal catalysts, the relationship between the intrinsic catalytic activity of N-carbon and the metal catalysts with N-carbon as support materials. The nanostructure of N-carbon and how to control the nanostructure in desirable state are also important and challenging. Theoretical calculations with

modern computers have shown to be powerful in searching novel electrocatalysts [189–191] and study the basic science behind the electrocatalysis [192], which have also been employed in studying N-CNT properties [54,193,194]. Theoretical calculations could be and should be employed in studying N-carbon-based catalysts.

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